

Transport and dissolution of ethanol and ethanol-blended gasoline in the subsurface



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Thank you!

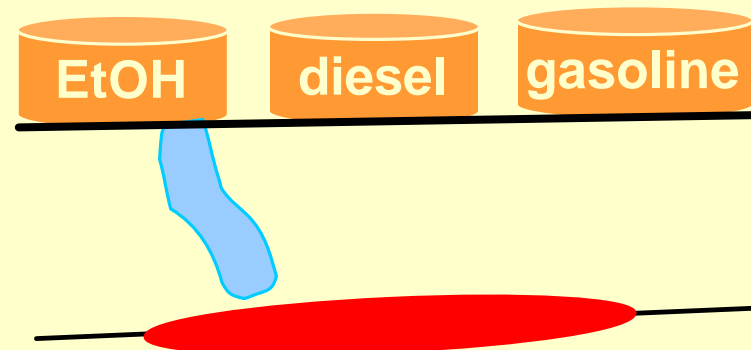


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 - Steven Heermann
 - Cory McDowell

Potential Spill Scenarios

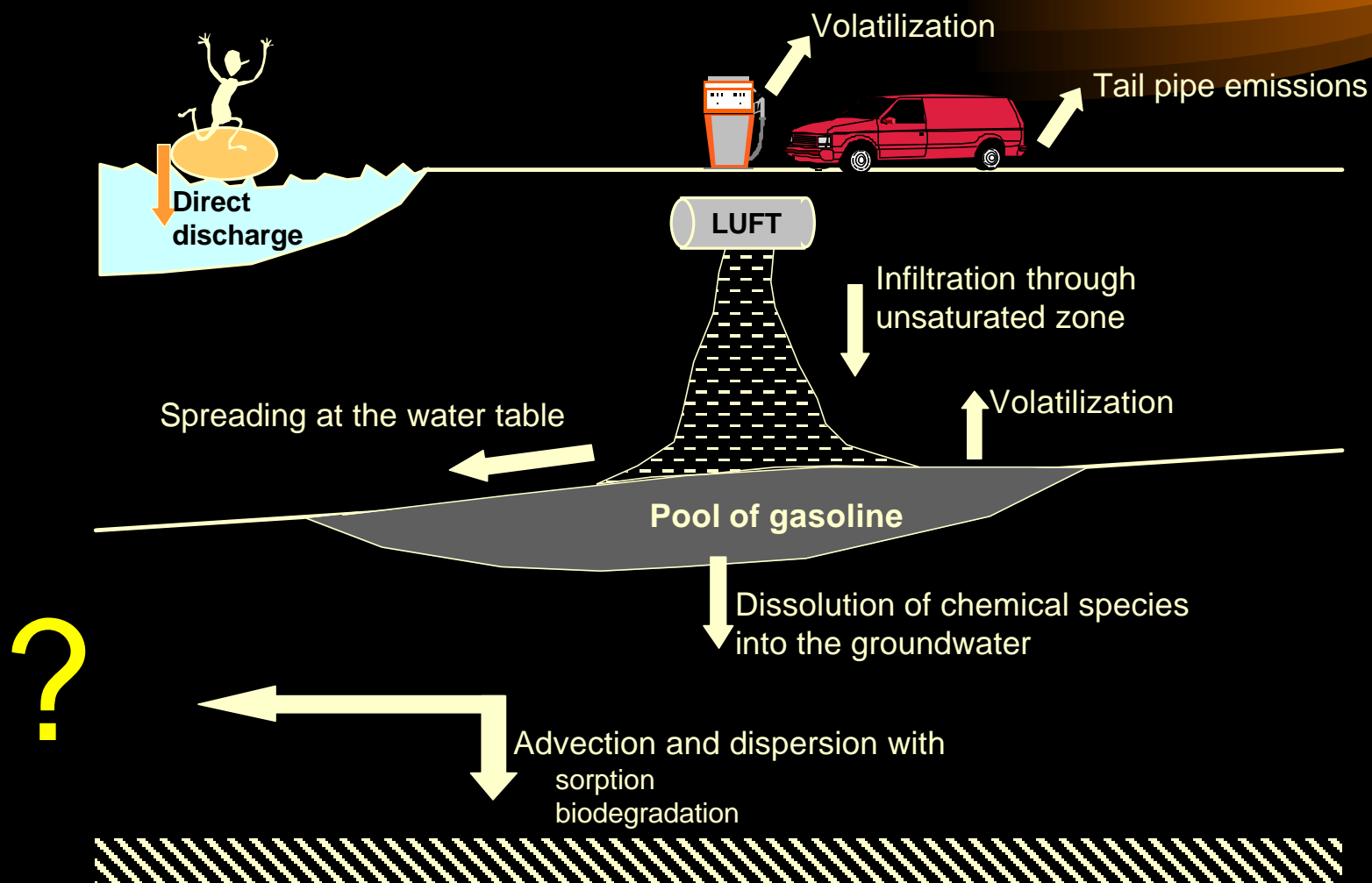


**Gasohol from LUFT
and trucks**



**Denatured ethanol at
bulk storage terminals**

Fate in the Environment

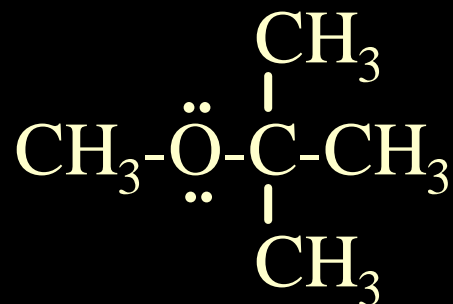


Molecular structure very revealing

Hexane

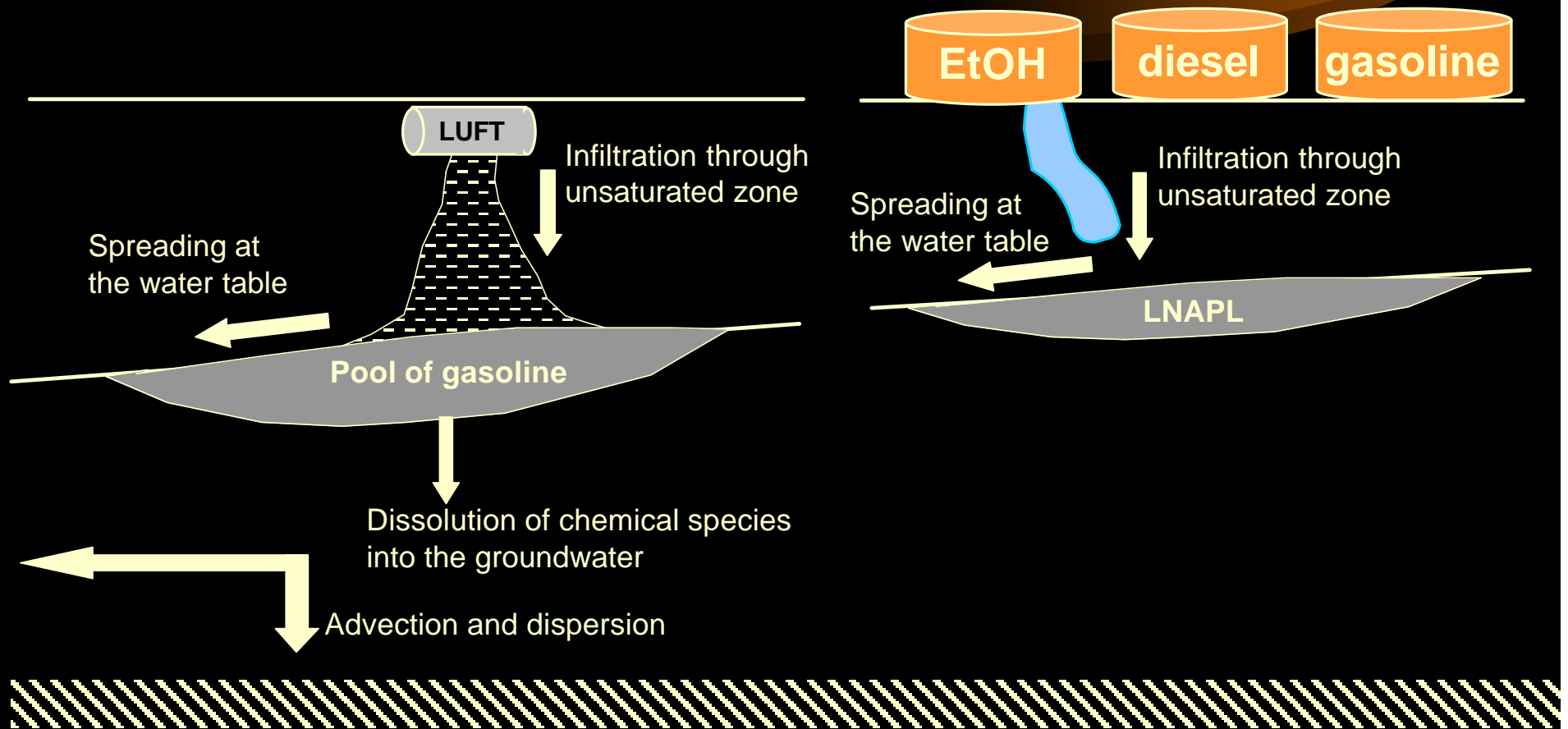
MTBE

Ethanol



What are the difference in
solubility
volatility
biodegradation???

Focus of Our Work



Abiotic Properties



- Hydrophilic characteristics of ethanol affect two chemical properties
 - Interfacial tension
 - Cosolvency

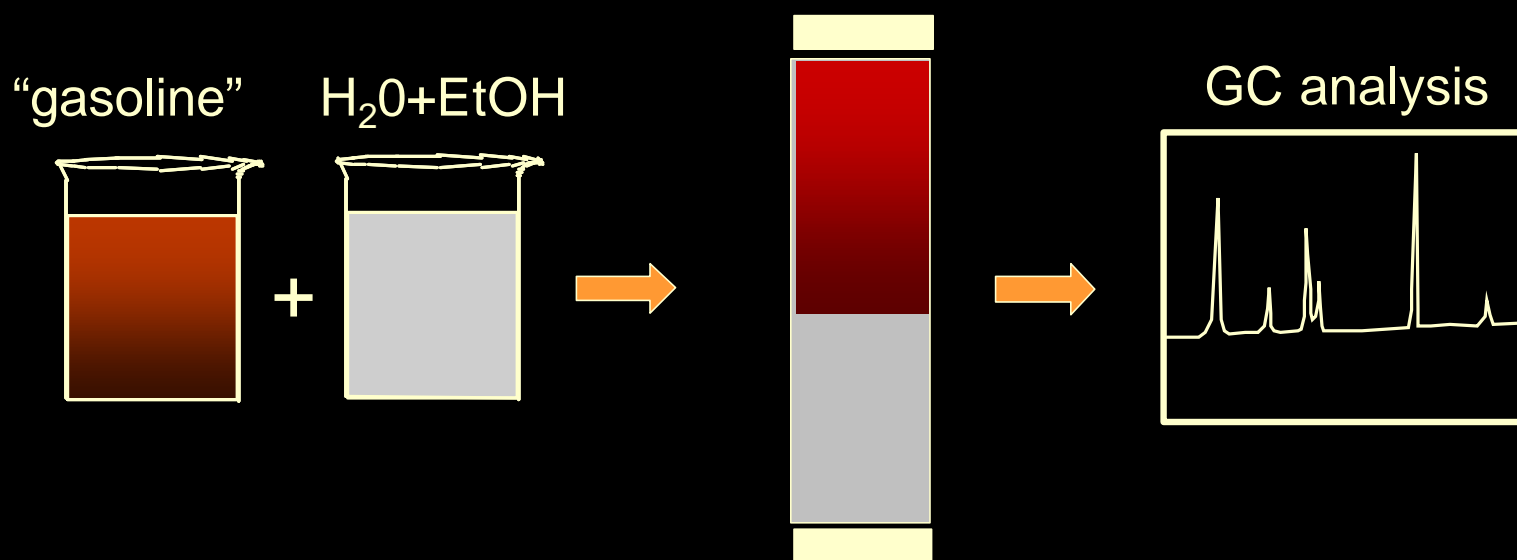
Cosolvency



- Adding ethanol to water reduces the importance of hydrogen bonding in the aqueous phase making it less polar.
- Increased solubility of BTEX
 - Higher concentrations
 - Less retardation

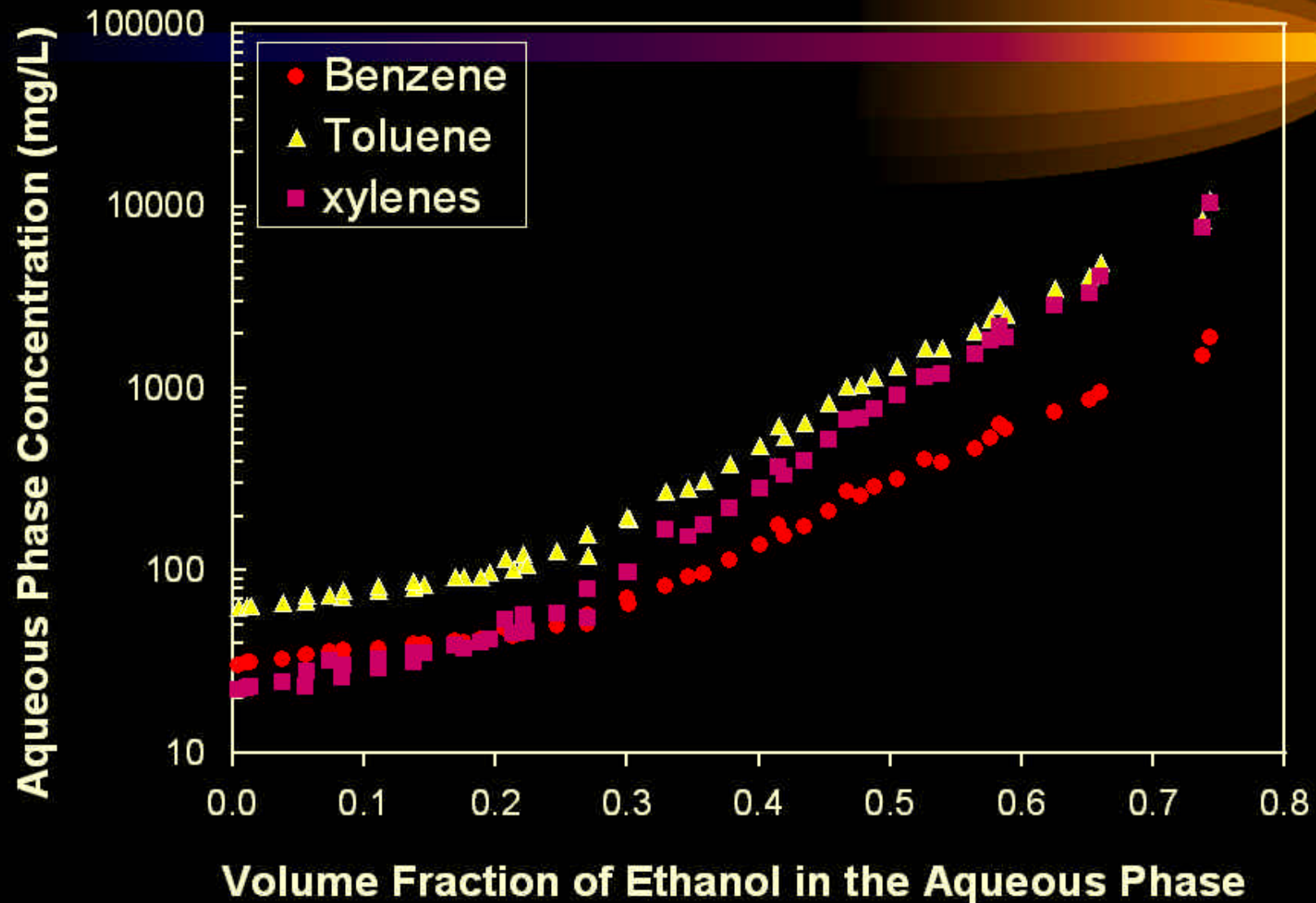
Experimental Methods

- Batch equilibrium experiments
 - surrogate gasolines (alkane + aromatic(s))
 - Philip's California Certified gasoline, "C2"

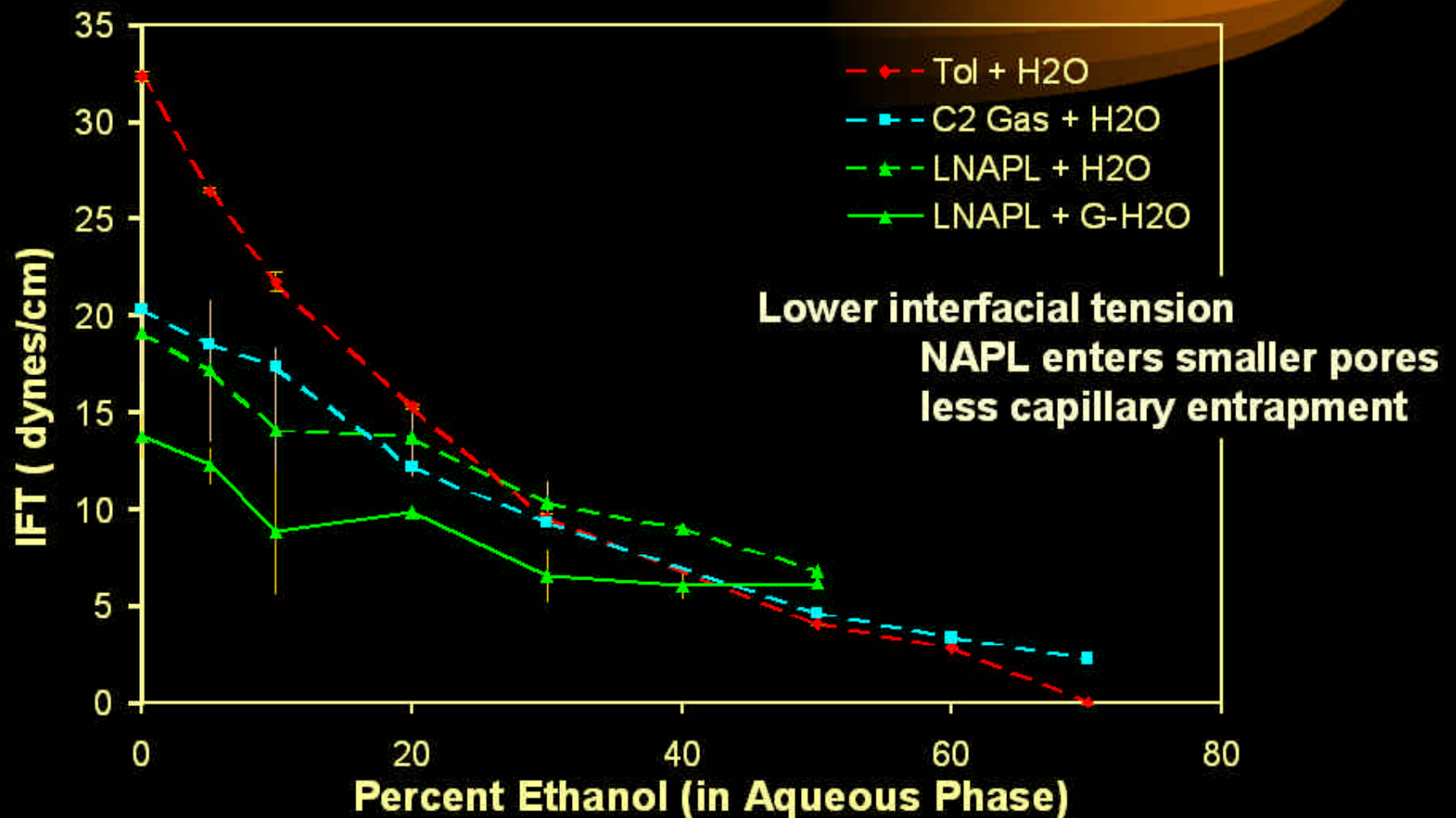


- Concentrations and densities measured

Cosolvency - C2 gasoline



Interfacial Tension

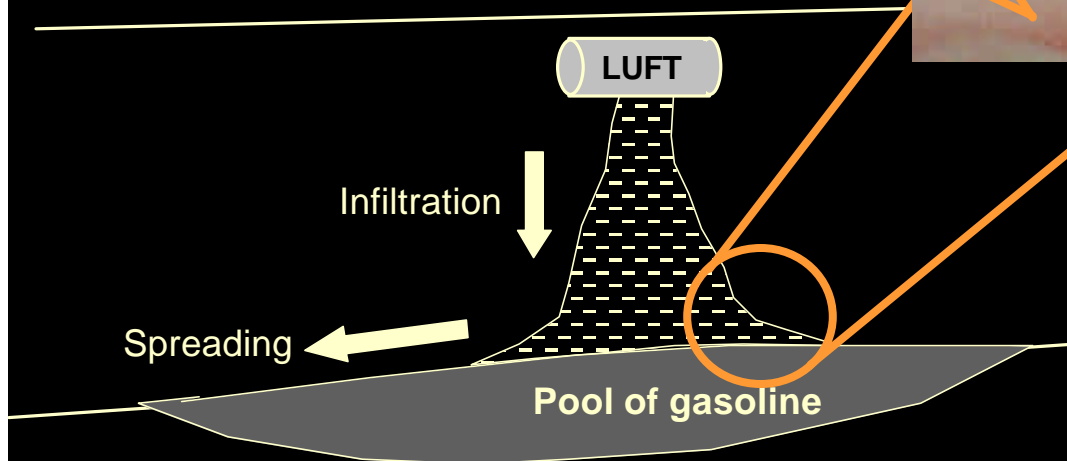
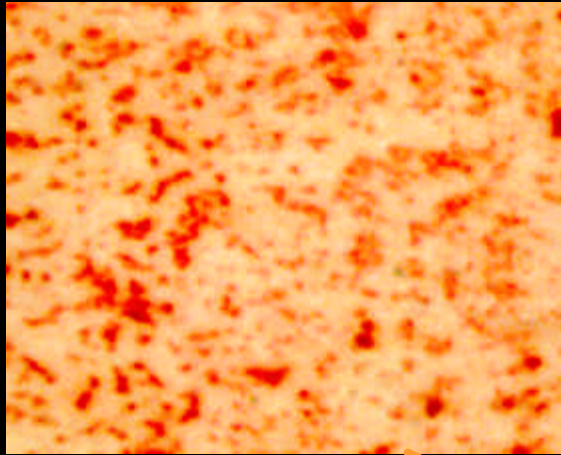


Focus of Our Work



- **Infiltration and spreading** of ethanol and ethanol-blended gasoline in vadose zone
- **Dissolution** of BTEX from the gasoline pool
 - Thermodynamic equilibrium - gasoline-ethanol-water
 - Rates of dissolution

Infiltration and spreading



Effects of added ethanol

Property Changes

Interfacial tension decreases

Increased solubility of NAPL

Potential Net Significance

Existing NAPL blobs dissolve and are mobilized

Reduction in capillary forces and capillary entrapment

Redistribution of NAPL

Example –

Ethanol spill into NAPL-contaminated soil

Observations – Gasoline Spill



Gasoline spill- spreading dominated by gravity and capillary action

Observations – Subsequent EtOH Spill

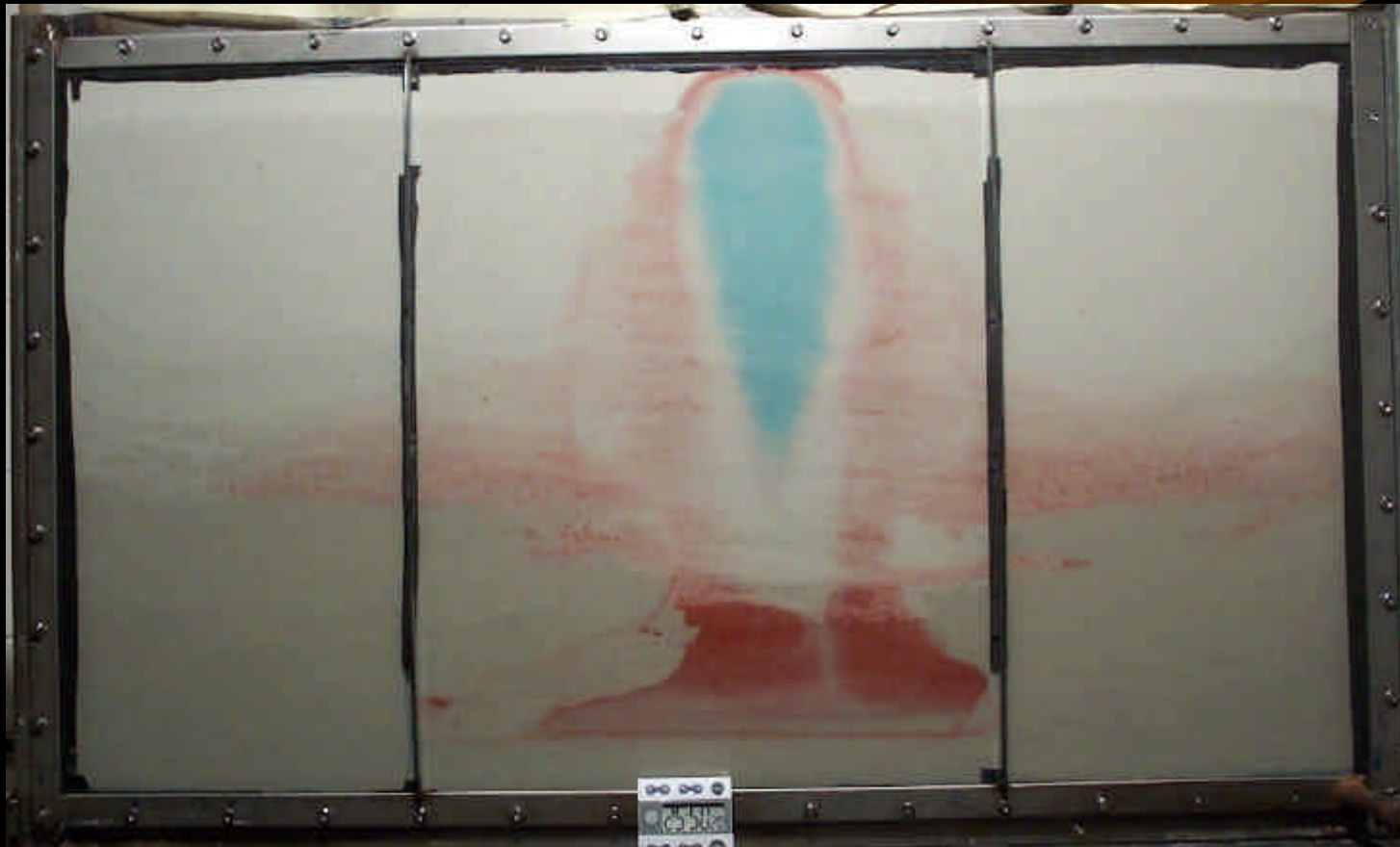


**Ethanol spill – gasoline dissolves
and spreads ahead of ethanol front**

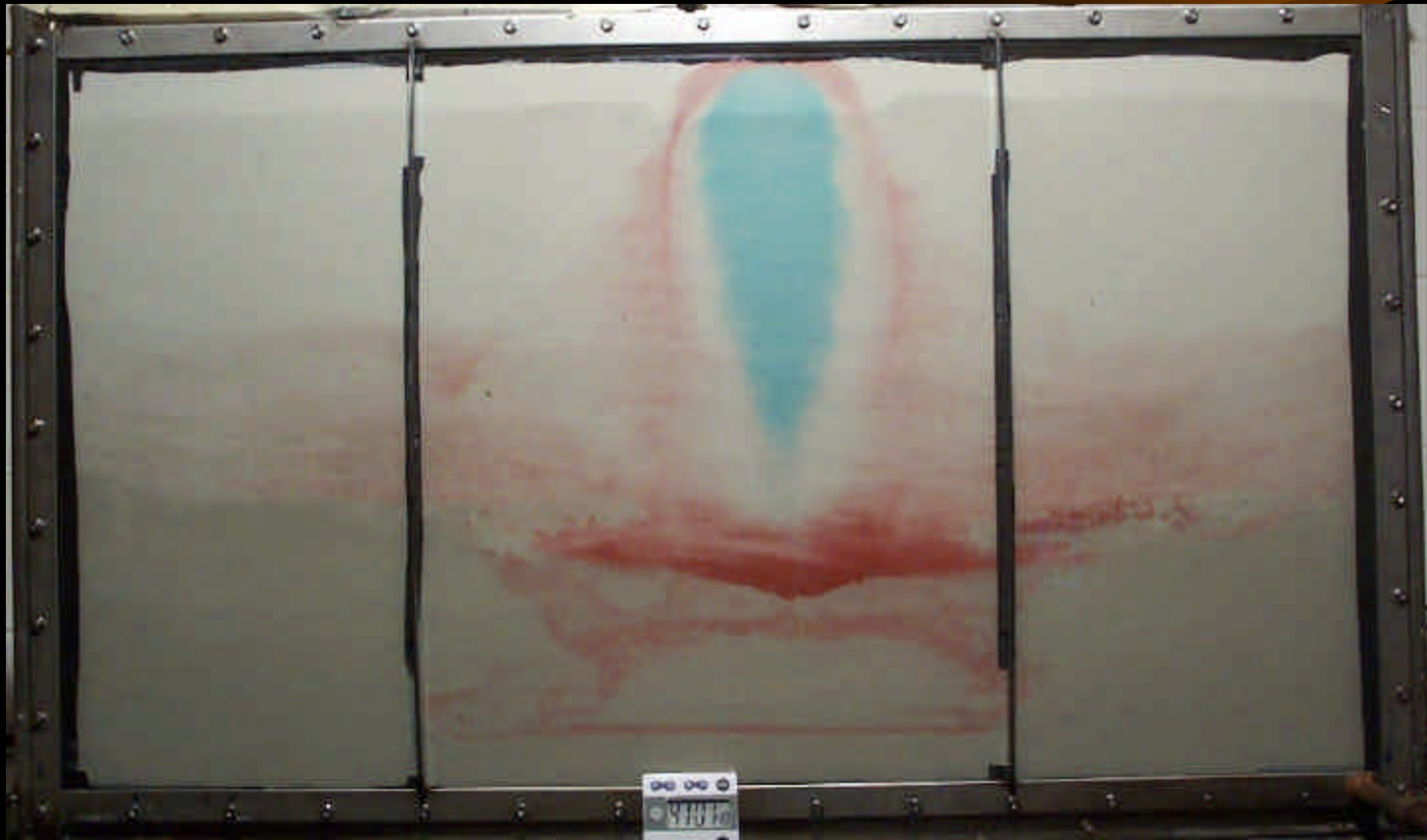
Ethanol does not spread by capillary action
Gasoline continues to move in advance of ethanol front
Capillary fringe is depressed



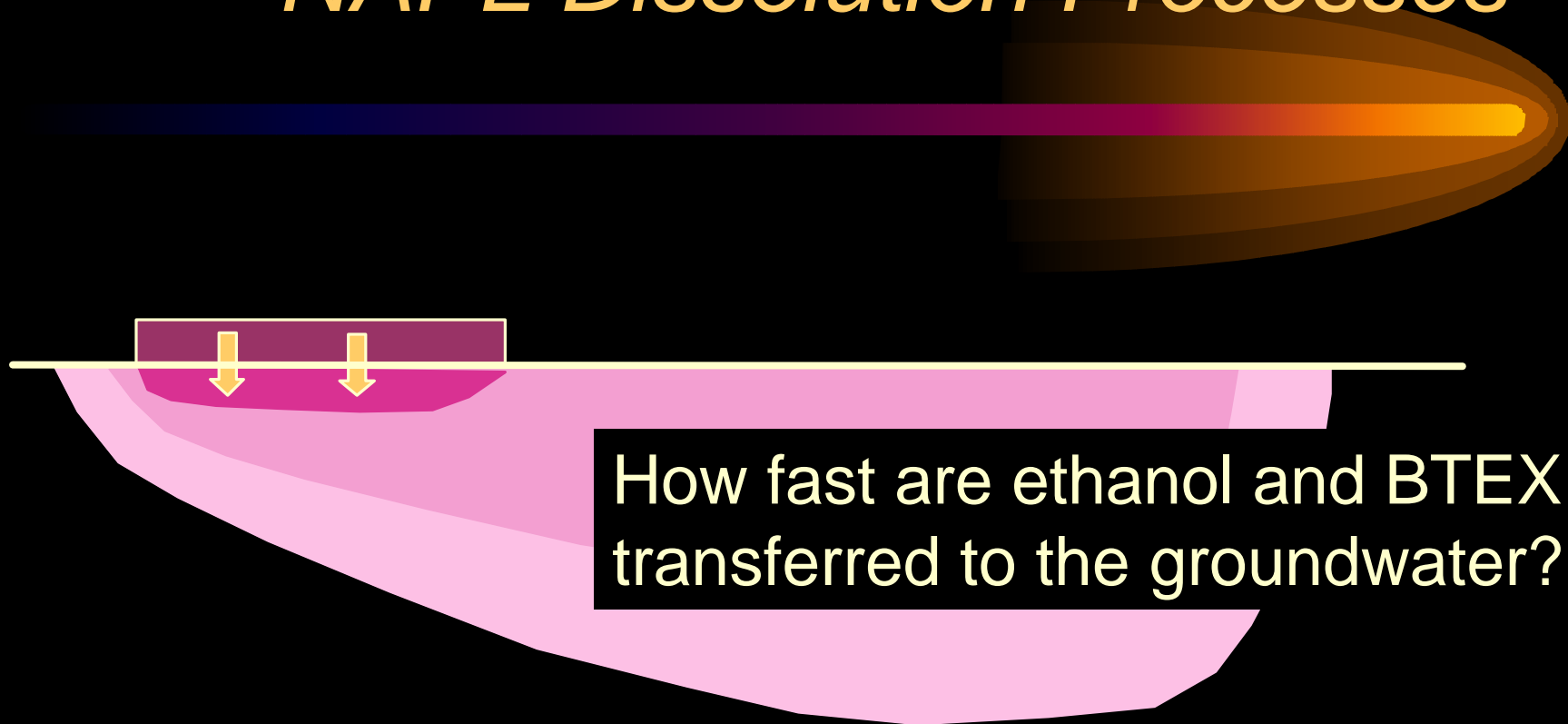
**Significant reduction of gasoline in vadose zone
Spreading of gasoline into saturated zone**



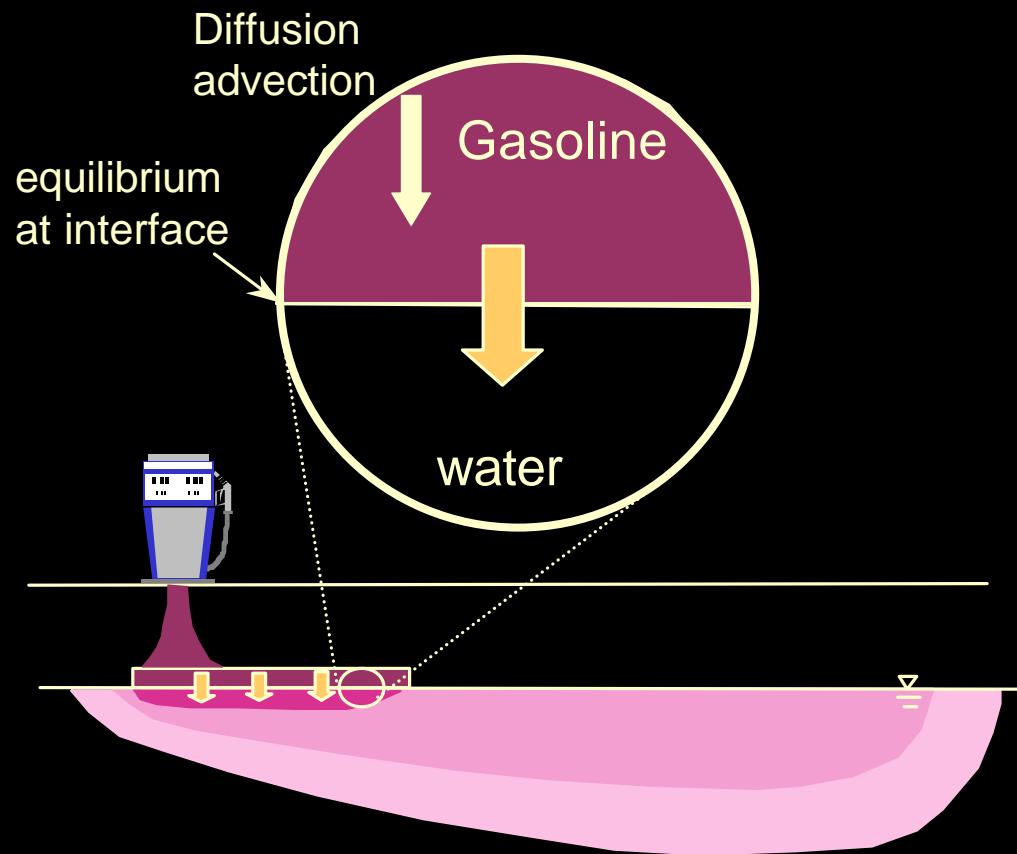
**As ethanol concentration decreases,
Capillary fringe rebounds
Increase in LNAPL saturation at the capillary fringe
Smearing of residual saturation in the saturated zone**



NAPL Dissolution Processes



Changes in the Gasoline Pool



Property Changes

Interfacial tension decreases

Composition of gasoline as ethanol leaches

Altered equilibrium condition

Potential Net Significance

Reduction in capillary forces

Concentration at source increased

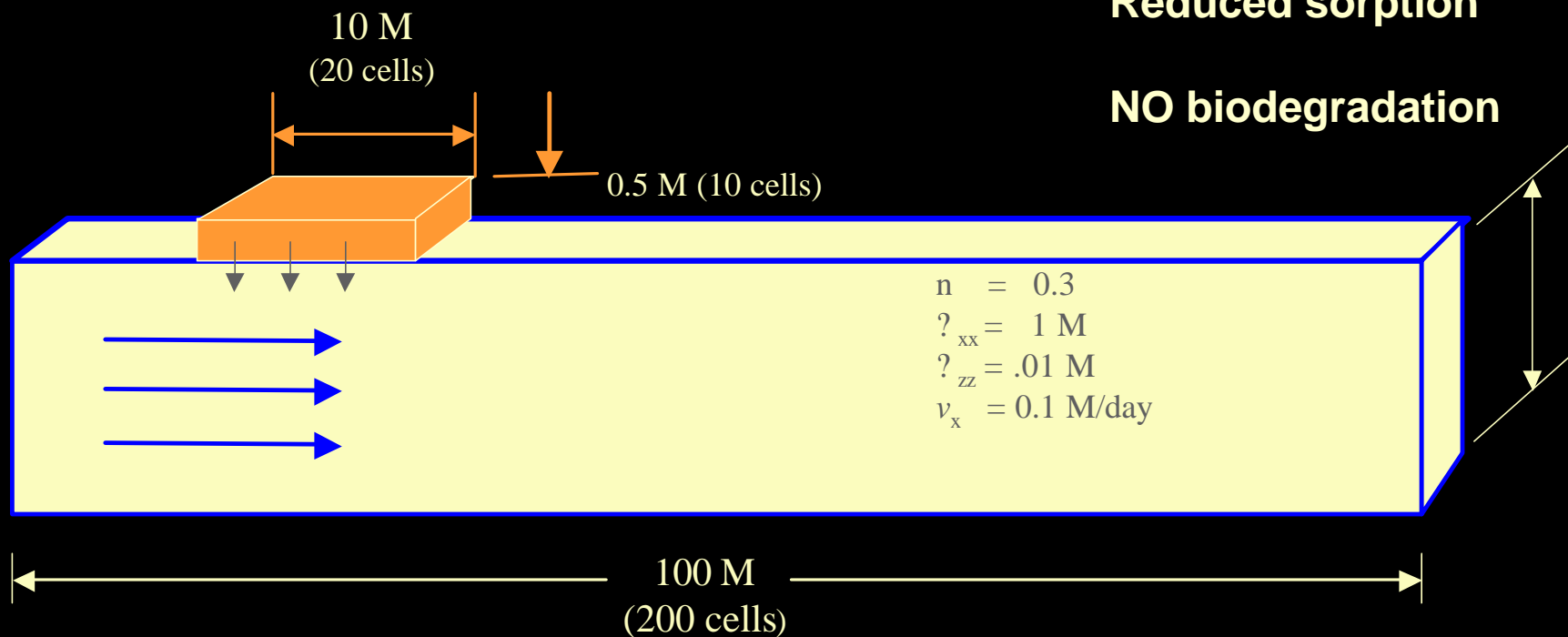
EtOH

BTEX

Modeling Efforts

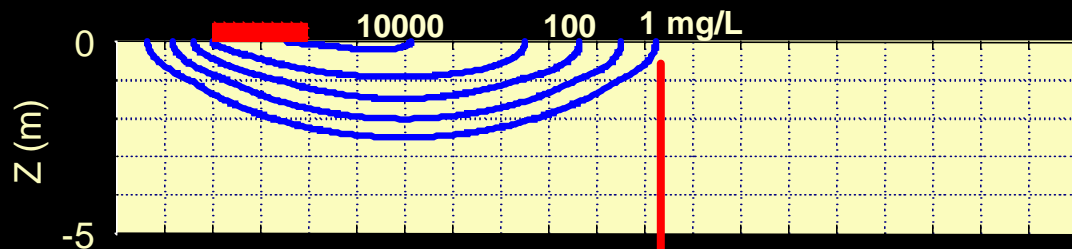
Cosolvency
Dissolution rates
Reduced sorption

NO biodegradation



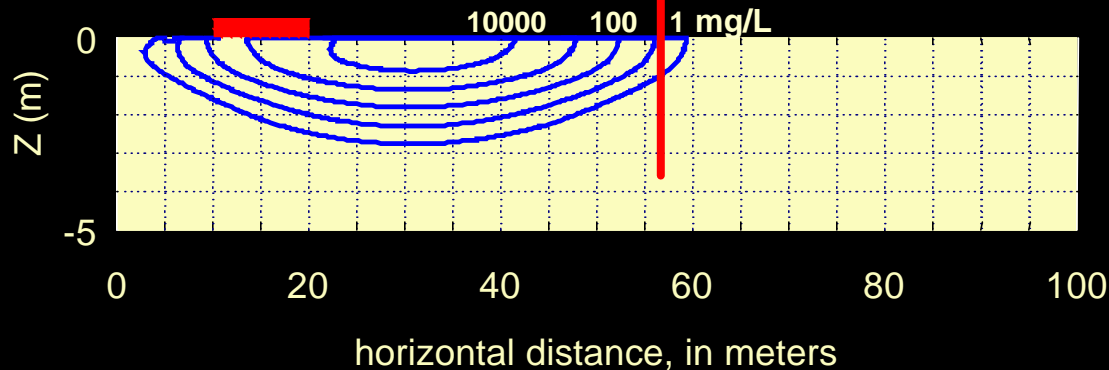
Modeling Results

Slow Dissolution Rates



Faster Dissolution Rate

(no rate limiting transport processes in gasoline)

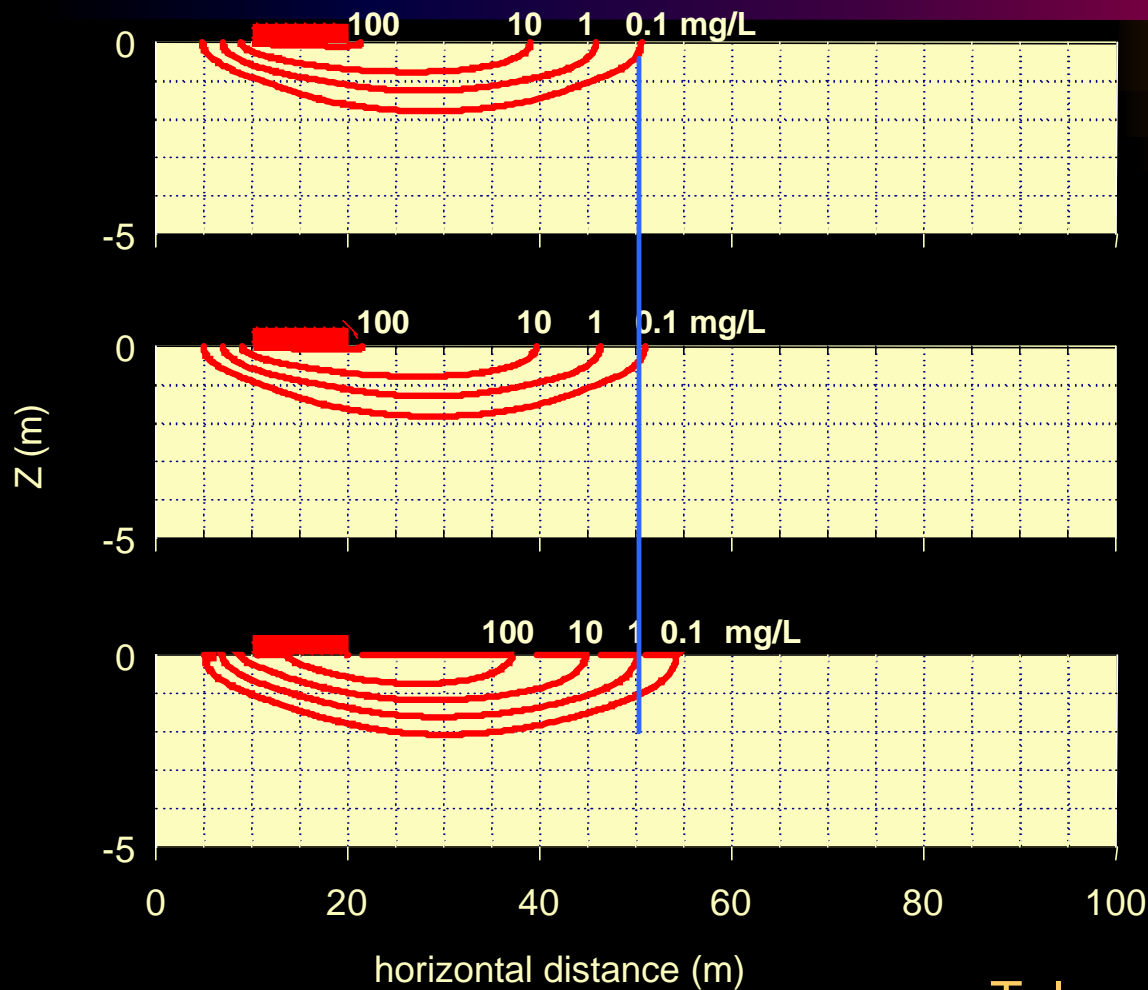


Explanation

- Gasoline pool:
 - 20 wt% ethanol
 - 16 wt% toluene
 - 64 wt% *n*-heptane
- Aqueous ethanol concentrations (mg/L)

Ethanol Concentrations (90 days)

Modeling Results



- no ethanol in gasoline

- 20 % etoh in gasoline;
- Slow mass transfer rates

- 20 % ethanol in gasoline;
- Fast mass transfer rates

Toluene Concentrations (90 days)

Modeling Predictions



- Slow mass transfer
 - negligible increase in BTEX mass transfer due to ethanol
- Faster mass transport
 - ethanol mass transfer rates are higher
 - total travel distance is slightly longer
 - cosolvency effect is sufficient to substantially increase BTEX concentrations in aquifer with 20% etoh in gasoline.

Summary

- LUFT spill events
 - Cosolvency and dissolution rates do not appear to have a significant impact on BTEX plumes
 - Uncertainty in rate of dissolution – but is it a significant issue?
 - Vadose zone issues still being investigated
- Ethanol spill events
 - Lowered interfacial tension greatly affects distribution of NAPL
 - Cosolvency effects result in significant increase in BTEX following ethanol spill

Research Needs



Individual processes studied in the laboratory
have to get *integrated* to understand net impacts

- Computer modeling
- Field-scale spill study